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Baker

A Search for Potash

A SEARCH FOR POTASH

BY

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Clifford

THESIS

FOR THE

DEGREE OF BACHELOR OF ARTS

IN

GENERAL SCIENCE

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

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DEGREE OF BACHELOR OF ARTS

in

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376637

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A Search For Potash.

Introduction.

There is scarcely any chemical problem which stares the American chemist in the face more at the present time than the potash situation. It is true that the outlook is much more encouraging than it was six months ago, due largely to the development of the Pacific Coast kelp beds and the saline deposits in the western states.

Until the opening of the great European war immense quantities of potassium salts were annually imported into this country from Germany, of which much was used in agriculture, as well as for chemical laboratories and industries.[1] The imports were about one-fourth in 1915 what they were in 1913, the last normal year and the import of kainite and manure salts were about three percent of those in 1913. ALL the imports of potash salts taken together in 1915 amounted to about one-tenth of the recent imports under normal conditions.

Potash salts[2] imported for consumption into the United States, 1912 - 1915.

1912		1913	
Quantity Pounds	Value	Quantity	Value
622,179,164	$10,692,285	612,514,916	$10,805,720
1914		1915	
485,818,459	$8,743,973	170,555,450	$3,765,224

1&2 U.S. Geological Survey, Potash Salts. (1915) 2 96

Since the domestic scarcity of potash salts has been felt there has been a great increase in the prices of these compounds.[3] From a normal price of $35 to $40 a ton for high grade agricultural salts prices have advanced steadily until in the spring of 1916 chloride and sulphate were quoted at ten times the above figures.[4] In April 1916 chloride was quoted at $425 a ton and sulphate from $350 to $400 a ton.

In the light of these astonishing facts the need for the production of potash and potash salts in this country has been keenly felt, and as a result much investigation has been carried on by the government, individuals and private industries, in the hope of obtaining these products on a commercial scale.

The following investigations show some of the possibilities which might be so utilized.

History of the Potash Situation.

About sixty years ago potash and potash salts were produced from wood ashes. The woods mostly used for this purpose were Elm, Birch, Larch and Maple. Hard woods were found to contain more potash than the softer varieties. This was a rather extravagant means of obtaining potash salts, even though the potash was easily leached from the ashes, but it was carried on to some extent on a commercial basis.

From the time when the Strassfurt beds were discovered in Germany, this industry gradually diminished in this country,

3 U.S. Geol. Survey. Potash Salts. (1915) 2, 95

4. Ibid.

until at the present time it is practically dead. The price for which potash salts could be obtained was so much less than the cost of production in this country that this industry has been almost entirely discontinued.[5] At the opening of the European war the potash salts produced in this country was only about one percent of the potash imported.

Now, again, we are facing a new era in the production of these products. The Germans have refused to export any potash to this country due to its increased use at home in the war, and the breaking off of relations with this country.

It is this present situation, that of being unable to obtain these products from Germany that is awakening the American chemists along this branch of chemical industry.

The demand for potash salts is daily increasing and it is the hope that the industries now engaging in their production will be able to produce them commercially not only in war times, but at such a cost that they may continue in normal times.

Possible Sources of Potash in the United States.

Kelp.-- The Pacific coast kelp beds are probably the most promising source for potash salts at the present time in this country. Different varieties vary in their potash content. Analysis of the dried plants show:

5. Jour. Ind. and Eng. Chem. Vol. 9 No. 5 pg. 473

	Alaria fistulosa	Macrocystis pyrifera	nereocystis lentkeana
Total Sol. Salts[6]	24.4%	30.00	46.9
K_2O	.91	12.59	20.1
I	Trace	.23	.13
n	2.6	1.57	1.9
ash	7.5	5.9	4.2

Seven concerns have installed plants for carrying on this great industry, that of extracting potash salts from kelp, among which are the Hercules Power Company, Swift and Company, the packers, National Chemical Company and others.

Bitterns.--

The Searles Lake in California has a specific gravity[7] of 1.2974. The bitterns which are concentrated by artificial evaporation contain rather large quantities of potassium salts, especially the chloride. Another such lake is the Owens lake in California.

An approximate total content of chlorine, sodium, potassium etc. in the water of Owens Lake, California.[8]

	Short Tons
Chlorine	40,000,000
Sodium	60,000,000
Potassium	3,360,000
Anhydrous boric acid (B_2O_3)	3,070,000
Total anhydrous salts	160,000,000

(See references on pg.5)

The Utah Chemical Company is now erecting a plant on the shores of the Great Salt Lake for the extraction of poatsh salts as a by-product.

Other bitterns worthy of mention are found in lakes of Texas, Oklahoma, Kansas. Colorado, Nebraska and New Mexico.

Saline Deposits.

Saline deposits including dry lakes, mud flats, alkali flats salt marshes, etc. have been found in the Great Basin. Veinsof alunite, an insoluble hydrous potassium sulphate,have been discovered in Utah, Nevada and Washington. These deposits show great promise of becoming commercially important as a source for potash salts.

Another form which is attracting much attention is silicate rock such as feldspar, leucite and sericite and greensand. Deposits of leucite rocks in Wyoming and sericite,in Georgia are spoken of as possible sources for potash. An [9] analysis of serite rock from Pickens County Ga., shows 10.75% K_2O. The greensand of New Jersey and Delaware 3.5% to 6.25% K_2O.

These last mentioned sources seem to be of some agricultural value, but not from the standpoint of the production of pure potash salts.

6. U.S. Dept of Agr. Report No. 100 , Potash from Kelp pg. 15-18
7. U.S. Geol. Survey. Potash Salts (1915) 2 , 100
8. Ibid. 2, 100 (1915)
9. Ibid. 2, 116.(1915)

Miscellaneous Sources.

Wood ashes are a possible source. Composition of wood ashes in 97 samples analyzed by Grossman:[10]

	Mean %	Maximum %	Minimum %
Potash	5.5	10.2	2.5
Phos. acid	1.9	4.0	0.3
Lime	34.3	50.9	18.0
Magnesia	3.5	7.5	2.3

The wastes from saw mills offer a possible source. Millions of pounds of saw dust are wasted yearly in our western saw mills The brush might also be utilized.

By- products from different industries offer other sources. Molasses from distillery waste when transformed into a dry powder contains 9% K_2O.[11] Potash is now being produced in several cement and lime factories as a by-product.

S.W. Sinsheimer[12] has invented a process for the recovery of nitrogen and potash from the concentrated molasses obtained from the manufacture of sugar from sugar beets.

The outlook now is rather favorable, for many investigations have been and are being made at the present time along the line of the production of potash salts commercially from the above mentioned sources, and plants for such production are fast being built and we look with hope upon these sources and other sources that may be discovered.

10. Met. and Eng. Chem. Nov. 15, 1915. pg. 841-46
11. Ibid. Oct. 15, 1915 pg. 760
12. U.S. Geol. Survey. Potash Salts part 2, pg. 126

precipitate joined with the preceeding one. The total precipitate was then dried for one hour at 100°- 140°C and the watch glass with the precipitate placed in a dessicator for one hour, when it was weighed. From the weight of $K_2Pt\ Cl_6$, the weight of potash salts was determined upon the basis of K_2O.

A comparison of the two methods may be shown from the results obtained from the work on banana stalks.

	% K_2O in air dry stalk
K_2O from laeching of air dry stalks	1.22 %
K_2O " " " ash from "	9.08 %

Further leachings gave corresponding small amounts of potash salts.

Experimental.

In these investigations the chlorplatinate method has been used throughout. Two different processes however, were thoroughly tried out.

The first, consisted of leaching the air dry substance to be tested for potash, for about two weeks and testing the extract thus obtained. This method failed however, to remove but a small percentage of the potash salts present and was discontinued as impracticable .

The second method consisted in igniting the air dry sample in a weighed container until the ash was free from all form of carbonaceous material. The percentage ash was obtained at this point. The ash was then treated with excessive amounts of hot water and leached for 48 hours, when the insoluble ash was filtered off by suction. The remaining ash was washed repeatedly with hot water to insure as nearly as possible a complete leaching out of all potash salts. An aliquot part of the filtrate was concentrated and made acid with a few drops of hydrochloric acid. To the solution was added enough 10% platinum chloride solution ($PtCl_4$) to insure complete precipitation of the sodium and potassium salts. The solution was then evaporated to dryness as slowly as possible on a water bath. The precipitate was transfered to a filter and washed repeatedly with anhydrous methyl alcohol, CH_3OH, to insure a complete removal of sodium salts.As nearly completely as possible the precipitate was transfered to a weighed watch glass. The remaining precipitate was dissolved in hot water and again evaporated to dryness and the

Table I.

K_2O in Water Plants.

Plant Tested	Botanical Name	Locality Grown	Percentage Ash
Hornwort	Ceratophyllum Demersum	Holland, Mich.	41.06
Under Water Plant	Potamogeton sp.	Alpena, Mich.	27.17
White Water Lily	----------	Alpena, Mich.	.12
Yellow Pond Lily	----------	Alpena, Mich.	12.06
Small Leaved Pondweed	Potamogeton sp.	Alpena, Mich.	30.51
Stonewort	Chara	Alpena, Mich.	50.29
Knot Weed	Potamogeton sp.	Alpena, Mich.	26.19
Illinois Pond Weed	Potamogeton Illinois	Alpena, Mich.	31.08
Northera Pondweed	Potamogeton sp.	Alpena, Mich.	33.01
Long Leaved Pondweed	Potamogeton Americanus	Holland, Mich.	29.5
Timber Moss and Roots	----------	Springfield, Mo.	17.91
Pickerel Weed	----------	Portland, Maine	12.65
Arrow-Head	----------	Portland, Maine	11.82
Pond-Weed	Potamogeton sp.	Portland, Maine	22.67
Eel Grass	----------	Portland Maine	18.42
Floating Pond Moss	----------	Bement, Ill.	63.00
Bull Rushes	----------	Bement, Ill.	36.54
Wild Swamp Grass	----------	Bement, Ill	9.86
Rag Weeds	----------	Bement, Ill	5.61

Percentage K_2O in Ash	Percentage K_2O in air dry sample
2.15	.89
2.29	.62
8.3	.099
5.49	.65
1.12	.34
.22	.13
1.59	.42
1.24	.39
1.47	.39
3.09	.91
4.69	.83
6.66	.84
16.30	1.93
4.39	.99
8.18	1.51
.11	.069
1.48	.54
1.73	.17
4.13	1.91

Table II.

K_2O in Waste Products.

Substance	Locality Grown	Percentage Ash	Percentage K_2O in Ash	Percentage K_2O Air Dry Sample
Banana Stalks	----------	20.11	45.17	9.08
Sunflower Stalks	Urbana, Ill	3.66	3.45	.13
Corn Stalks	Bement, Ill.	10.03	2.79	.28
Cotton Stalks	Urbana, Ill.	8.46	20.84	1.76
Tobacco Stems	Urbana, Ill.	19.19	29.58	5.83
Cigar	----------	17.9	35.01	6.29

Table III.

Sugar Waste Determinations.

		Percentage Ash	Percentage K_2O in Ash	Percentage K_2O IN crude sam-	Sp. Gr.
St, Louis Sugar Co.	Holland, Mich.	3.13	31.8	.995	1.391
Owasso	Owasso, Mich.	3.57	36.46	1.113	1.423

The water content in the former was approximately 25-30 %

and in the latter , 20-25 %.

Discussion of Results and Conclusions.

1. From the above results it is clearly seen that fresh water plants, in general, do not furnish a source for potash on a commercial basis.

2. It is also evident that floating plants and leaves contain much less potash than those plants rooted in the beds of rivers and lakes.

3. Certain waste products seem to be commercially important in the potash industry. Banana stalks contain large amounts of potash salts, and thousands of them are discarded daily in the cities.

Cotton and tobacco stems also contain large amounts of potash salts. As neither of these products are used to any appreciable extent it may be suggested that they might be so treated as to become a commercial source of potash.

The syrups from the beet sugar industries contain rather large amounts of potash salts. These syrups by a destructive distillation can be separated into volatile and non-volatile valuable products. The potash content of these syrups, until recently has totally been ignored. They, however, appear to also be important for their potash content which might be extracted for commercial gains.

Note: I wish to thank Dr. B.S.Hopkins for his many suggestions and valuable assistance which he has given in the preparation of this thesis.

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